

Time-convolutionless master equation for mesoscopic electron-phonon systems

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The time-convolutionless master equation for the electronic populations is derived for a generic electron-phonon Hamiltonian. The equation can be used in the regimes where the golden rule approach is not applicable. The equation is applied to study the electronic relaxation in several models with the finite number normal modes. For such mesoscopic systems the relaxation behavior differs substantially from the simple exponential relaxation. In particular, the equation shows the appearance of the recurrence phenomena on a time-scale determined by the slowest mode of the system. The formal results are quite general and can be used for a wide range of physical systems. Numerical results are presented for a two level system coupled to a Ohmic and super-Ohmic baths, as well as for a model of charge-transfer dynamics between semiconducting organic polymers.

I. INTRODUCTION

The Pauli master equation and the Redfield equation have long been applied to the study of relaxation dynamics in electronic systems [1, 2, 3]. These equations were originally derived using semi-heuristic arguments. However, with the advent of projection operator techniques in 1960's [4, 5, 6] it became clear that such master equations could be obtained from formally exact generalized master equations through a series of well defined approximations. Such approximations are usually justified when the system of interest is coupled to a thermostat with a large number of degrees of freedom. In this limit, the resultant transition probabilities in the Pauli master equation are identical to those obtained by the less rigorous golden rule approach [2].

The case when the thermostat is mesoscopic (i.e. with a finite number of modes) is less well studied. In general, for this case the time independent transition probabilities of the golden rule type may not be well defined since the kernels of the generalized master equations do not vanish in the limit $t \rightarrow \infty$. Our goal in this paper is to develop a time-convolutionless generalized master equation suitable for a mesoscopic electron-phonon system using the fact that this equation becomes formally exact for arbitrary system sizes. In contrast to the derivation of the Pauli master equation, the only approximation that we will use is that of weak coupling. As a result we will arrive at a master equation with time dependent rate coefficients.

II. HAMILTONIAN AND THE INITIAL STATE

A wide class of the electron-phonon systems can be described by the following Hamiltonian ($\hbar = 1$)

$$H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{nmi} g_{nmi} |n\rangle\langle m| (a_i^\dagger + a_i) + \sum_i \omega_i a_i^\dagger a_i. \quad (1)$$

Here $|n\rangle$'s denote electronic states with vertical energies ϵ_n , a_i^\dagger and a_i are the creation and annihilation operators for the normal mode i with frequency ω_i , and g_{nmi} are the coupling parameters of the electron-phonon interaction which we take to be linear in the phonon normal mode displacement coordinate.

We can separate H into a part that is diagonal with respect to the electronic degrees of freedom,

$$H_0 = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{ni} g_{nmi} |n\rangle\langle n| (a_i^\dagger + a_i) + \sum_i \omega_i a_i^\dagger a_i, \quad (2)$$

and an off-diagonal part V

$$V = \sum'_{nmi} g_{nmi} |n\rangle\langle m| (a_i^\dagger + a_i), \quad (3)$$

where the prime at the summation sign indicates that the terms with $n = m$ are excluded. This separation is useful for the following two reasons. First, in many systems only off-diagonal coefficients g_{nmi} are small compared to g_{nni} . Hence, V can be treated as a perturbation. Second, for many cases of interest, the initial density matrix commutes with H_0 . In this case, the separation gives simpler forms of the master equations.

For further analysis it is convenient to diagonalize H_0 with respect to the normal mode degrees of freedom. This is achieved with the unitary operator

$$U = e^{-\sum_{ni} \frac{g_{nni}}{\omega_i} |n\rangle\langle n| (a_i^\dagger - a_i)} = \sum_n |n\rangle\langle n| e^{-\sum_{ni} \frac{g_{nni}}{\omega_i} (a_i^\dagger - a_i)} \quad (4)$$

as

$$\tilde{H}_0 = U^{-1} H_0 U = \sum_n \tilde{\epsilon}_n |n\rangle\langle n| + \sum_i \omega_i a_i^\dagger a_i, \quad (5)$$

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where the renormalized electronic energies are

$$\tilde{\epsilon}_n = \epsilon_n - \sum_i \frac{g_{nni}^2}{\omega_i}. \quad (6)$$

Applying the same unitary transformation to V gives

$$\begin{aligned} \tilde{V} &= U^{-1} V U \\ &= \sum'_{nmi} \left(g_{nni} |n\rangle \langle m| \left(a_i^\dagger + a_i - \frac{2g_{nni}}{\omega_i} \right) \right. \\ &\quad \left. \times e^{\sum_j \frac{(g_{nnj} - g_{mmj})}{\omega_j} (a_j^\dagger - a_j)} \right). \end{aligned} \quad (7)$$

Introducing operators

$$M_{nni} = g_{nni} \left(a_i^\dagger + a_i - \frac{2g_{nni}}{\omega_i} \right) e^{\sum_j \frac{(g_{nnj} - g_{mmj})}{\omega_j} (a_j^\dagger - a_j)}, \quad (8)$$

we can rewrite \tilde{V} in a compact form as

$$\tilde{V} = \sum'_{nmi} |n\rangle \langle m| M_{nni}. \quad (9)$$

The similar unitary transformations were applied to the electron-phonon Hamiltonians before [7, 8]. As can be seen from Eq. 7, in the transformed picture the electronic transitions from state $|n\rangle$ to $|m\rangle$ are accompanied not only by the creation or annihilation of a single phonon of mode i but also by the displacements of all the normal modes.

Let us take for the initial density matrix

$$\rho(0) = |n\rangle \langle n| \frac{e^{-\beta(\sum_i \omega_i a_i^\dagger a_i + \sum_i g_{nni}(a_i^\dagger + a_i))}}{\text{Tr}(e^{-\beta(\sum_i \omega_i a_i^\dagger a_i + \sum_i g_{nni}(a_i^\dagger + a_i))})}, \quad (10)$$

where the electronic subsystem is prepared in a specific state $|n\rangle$ and the oscillators are in the displaced equilibrium configuration corresponding to this state. The transformed initial state $\tilde{\rho}(0) = U^{-1} \rho U$ has the form

$$\tilde{\rho}(0) = |n\rangle \langle n| \frac{e^{-\beta \sum_i \omega_i a_i^\dagger a_i}}{\text{Tr}(e^{-\beta \sum_i \omega_i a_i^\dagger a_i})}. \quad (11)$$

The electronic density matrix in the Eq. 10 commutes with unitary operator (4), hence its time evolution will be the same in both the transformed and the untransformed pictures. For the purpose of developing a perturbative theory, it is more convenient at this point to work in with the transformed operators.

III. MASTER EQUATION

We now use the projection operator formalism to obtain the master equation for the diagonal part of the electronic density matrix ρ^{el} [2, 3]. For a given projection operator \mathcal{P} and the initial total density matrix that satisfies $\rho(0) = \mathcal{P}\rho(0)$, $\mathcal{P}\rho(t)$ can be shown to satisfy at least

two different master equations: the Nakajima-Zwanzig (NZ) equation [4, 5, 6] and the time-convolutionless (CL) master equation [9].

$$\frac{\partial \mathcal{P}\rho}{\partial t} = - \int_0^t d\tau \mathcal{K}^{NZ}(t-\tau) \mathcal{P}\rho(\tau), \quad (12)$$

$$\frac{\partial \mathcal{P}\rho}{\partial t} = - \int_0^t d\tau \mathcal{K}^{CL}(\tau) \mathcal{P}\rho(t). \quad (13)$$

The explicit expressions for superoperators $\mathcal{K}^{NZ}(\tau)$ and $\mathcal{K}^{CL}(\tau)$ can be found in Ref. [3].

Even though Eqs. 12 and 13 are formally exact, it is impossible to calculate $\mathcal{K}^{NZ}(\tau)$ and $\mathcal{K}^{CL}(\tau)$ for most realistic systems. We will use the perturbation expansion of these superoperators. To the second order in the coupling constants

$$\mathcal{K}_2^{NZ}(\tau) = \mathcal{K}_2^{CL}(\tau) = \mathcal{P} \mathcal{L}_V e^{-i\mathcal{L}_0\tau} \mathcal{L}_V \mathcal{P}. \quad (14)$$

Here \mathcal{L}_0 and \mathcal{L}_V are the Liouville superoperators corresponding to \tilde{H}_0 and \tilde{V} whose action on some density matrix ρ is given by

$$\mathcal{L}_0 \rho = \tilde{H}_0 \rho - \rho \tilde{H}_0, \quad \mathcal{L}_V \rho = \tilde{V} \rho - \rho \tilde{V}. \quad (15)$$

In Ref. [3], Breuer and Petruccione show that to second order in the coupling constants, the convolutionless expression (Eq. 13) gives a better approximation to the exact solution than the Nakajima-Zwanzig equation (Eq. 12). It also has an additional mathematical convenience of being local in time. Therefore, in the following analysis we will use the convolutionless approach.

Since our initial state is given by Eq. 11 we will use the projection operator that acts on the total density matrix in the following way

$$\mathcal{P}\rho = \sum_n |n\rangle \langle n| \rho_{eq}^{os} \text{Tr}(|n\rangle \langle n| \rho), \quad (16)$$

where

$$\rho_{eq}^{os} = \frac{e^{-\beta \sum_i \omega_i a_i^\dagger a_i}}{\text{Tr}(e^{-\beta \sum_i \omega_i a_i^\dagger a_i})}. \quad (17)$$

Using the definition of $\mathcal{K}_2^{CL}(\tau)$ the following convolutionless equation is obtained for $P_n = \langle n | \rho_{el} | n \rangle$,

$$\frac{dP_n}{dt} = \sum_m W_{nm}(t) P_m - \sum_m W_{mn}(t) P_n. \quad (18)$$

The coefficients $W_{nm}(t)$ that are, in general, time dependent rates given by

$$W_{mn}(t) = 2\Re e \int_0^t d\tau \sum_{ij} \langle M_{nnmi} M_{mnj}(\tau) \rangle e^{-i(\tilde{\epsilon}_n - \tilde{\epsilon}_m)\tau} \quad (19)$$

where

$$\langle M_{nnmi} M_{mnj}(\tau) \rangle = \text{Tr} (M_{nnmi} M_{mnj}(\tau) \rho_{eq}^{os}) \quad (20)$$

and

$$M_{mnj}(\tau) = e^{i\tilde{H}_0\tau} M_{mnj} e^{-i\tilde{H}_0\tau}. \quad (21)$$

Due to the explicit form of operators M_{nmi} (Eq. 8) the calculation of the correlation functions in Eq. 20 can be reduced to the averaging of the displacement operators over the equilibrium ensemble (Eq. 17). After straightforward, but lengthy, calculations we obtain the principal result of this paper:

$$\begin{aligned} \langle M_{nmi} M_{mnj}(\tau) \rangle &= g_{nmi} g_{mnj} \\ &\times ((\Delta_{nmi}(\bar{n}_i + 1)e^{i\omega_i\tau} - \Delta_{nmi}\bar{n}_i e^{-i\omega_i\tau} + \Omega_{nmi}) \\ &\times (\Delta_{nmj}(\bar{n}_j + 1)e^{i\omega_j\tau} - \Delta_{nmj}\bar{n}_j e^{-i\omega_j\tau} + \Omega_{nmj}) \\ &+ \delta_{ij}(\bar{n}_i + 1)e^{i\omega_i\tau} + \delta_{ij}\bar{n}_i e^{-i\omega_i\tau}) q_{nm}(\tau) f_{nm}(\tau). \end{aligned} \quad (22)$$

Here

$$\Delta_{nmi} = \frac{(g_{nni} - g_{mmi})}{\omega_i}, \quad (23)$$

$$\Omega_{nmi} = \frac{(g_{nni} + g_{mmi})}{\omega_i}, \quad (24)$$

$$\bar{n}_i = \frac{1}{e^{\beta\omega_i} - 1}, \quad (25)$$

$$q_{nm}(\tau) = e^{i \sum_j \Delta_{nmj}^2 \sin \omega_j \tau}, \quad (26)$$

$$f_{nm}(\tau) = e^{-2 \sum_j (\bar{n}_j + \frac{1}{2}) \Delta_{nmj}^2 (1 - \cos \omega_j \tau)}. \quad (27)$$

In the case when all the diagonal electron/phonon terms vanish, $g_{nni} = 0$, the correlation functions in Eq. 22 reduce to those obtained within the golden rule approach [2]. It is clear from Eq. 22 that for systems with $g_{nni}/\omega_i \gg 1$ the golden rule approach is not applicable.

The qualitative behavior of the probabilities $P_n(t)$ depends on the explicit form of the time dependent rates $W_{mn}(t)$ in Eq. 18. Depending on a particular system, certain simplifications of $W_{mn}(t)$ are possible. In particular, for large systems we can expect the integrand in

Eq. 19 to decay to zero and, correspondingly, $W_{mn}(t)$ to become constant in the long time limit. If the typical electronic relaxation times are much longer then the decay rate of the integrand in Eq. 19, then the $W_{mn}(t)$ can be replaced by their time independent Markovian limits. Due to the rather complicated functional forms of $q_{nm}(t)$ and $f_{nm}(t)$ in Eq. 22 we could not obtain an explicit expression for $W_{mn}(t)$ in the Markovian limit. However, for models that satisfy the condition $\sum_j (\bar{n}_j + \frac{1}{2}) \Delta_{nmj}^2 \gg 0$ and with Δ_{nmi} taken as smooth function of i , we can approximate $f_{nm}(\tau)$ in Eq. 27 by a Gaussian, viz.,

$$f_{nm}(\tau) \approx e^{-a_{nm}\tau^2} \quad (28)$$

where

$$a_{nm} = \sum_j (\bar{n}_j + \frac{1}{2}) \Delta_{nmj}^2 \omega_j^2. \quad (29)$$

For $\omega_i\tau \ll 1$, we can also approximate the $\sin \omega_i\tau$ terms that appear in functions $q_{nm}(t)$ (Eq. 26) by $\sin \omega_i\tau \approx \omega_i\tau$ so that

$$q_{nm}(t) \approx e^{i\gamma_{nm}t}, \quad (30)$$

where

$$\gamma_{nm} = \sum_i \Delta_{nm}^2 \omega_i. \quad (31)$$

Under these approximations the long time (Markovian) limit of $W_{nm}(t)$ can be obtained as

$$\lim_{t \rightarrow \infty} W_{nm}(t) = \sum_{ij} L_{nmij}, \quad (32)$$

where

$$\begin{aligned} L_{nmij} &= g_{nmi} g_{mnj} \left(\Delta_{nmi} \Delta_{nmj} \left((\bar{n}_i + 1)(\bar{n}_j + 1) G_{nm}(\omega_i + \omega_j + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \right. \right. \\ &\quad + \bar{n}_i \bar{n}_j G_{nm}(-\omega_i - \omega_j + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) - (\bar{n}_i + 1) \bar{n}_j G_{nm}(\omega_i - \omega_j + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \\ &\quad \left. \left. - (\bar{n}_j + 1) \bar{n}_i G_{nm}(\omega_j - \omega_i + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \right) \right. \\ &\quad + \Delta_{nmi} \Omega_{nmj} \left((\bar{n}_i + 1) G_{nm}(\omega_i + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) - \bar{n}_i G_{nm}(-\omega_i + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \right) \\ &\quad + \Delta_{nmj} \Omega_{nmi} \left((\bar{n}_j + 1) G_{nm}(\omega_j + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) - \bar{n}_j G_{nm}(-\omega_j + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \right) \\ &\quad + \Omega_{nmi} \Omega_{nmj} G_{nm}(\gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \\ &\quad + \delta_{ij} (\bar{n}_i + 1) G_{nm}(\omega_i + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \\ &\quad \left. + \delta_{ij} \bar{n}_i G_{nm}(-\omega_i + \gamma_{nm} - \tilde{\epsilon}_n + \tilde{\epsilon}_m) \right), \end{aligned} \quad (33)$$

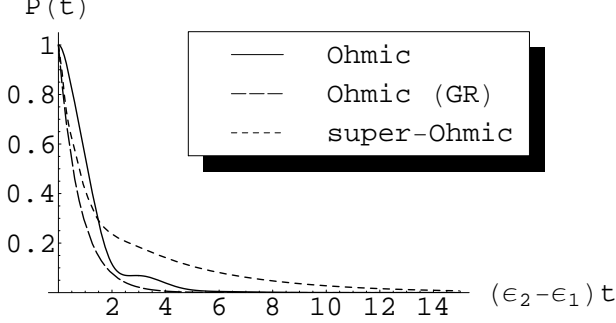


FIG. 1: The population of the excited state as a function of time for the 80 mode system with $\omega_j = A \sin(\frac{j\pi}{160})$. The solid line corresponds to $A = 10$, $\lambda = 0.1$, $p = -1/2$, and $\epsilon_2 - \epsilon_1 = 1$, the line of short dashes corresponds to $A = 10$, $\lambda = 0.2$, $p = 0$, and $\epsilon_2 - \epsilon_1 = 1$. The line of long dashes corresponds to the golden rule results for the Ohmic case. Temperature is 298 K for all cases.

with

$$G_{nm}(x) = \sqrt{\frac{\pi}{a_{nm}}} \exp\left(-\frac{x^2}{4a_{nm}}\right). \quad (34)$$

IV. RELAXATION IN MODEL ELECTRON-PHONON SYSTEMS

In what follows, we examine the solution of the Pauli equation for a number of model systems using the correlation functions (Eq. 22) defined above. We take two examples, one in consisting of a two state electronic system coupled to a single acoustic phonon branch with Ohmic and super-Ohmic couplings. The other taken from our recent work in describing secondary exciton formation at the domain boundary in organic polymer semiconductor heterojunctions. We also, then compare the results obtain using the present method to those obtained using Marcus' formulation of the rate-constant.

A. Ohmic vs. Super-Ohmic Coupling

As our first example we consider a system with two electronic levels coupled to N normal modes with frequencies $\omega_i = A \sin(i\pi/2N)$ with $i \in [1, N]$ that model the acoustic phonon branch. We will choose the coupling coefficients in the following form $g_{12i} = g_{21i} = g_{11i} = \lambda(\omega_i)^p$ and $g_{22i} = -\lambda(\omega_i)^p$, where λ and p are parameters. We will consider the cases of $p = -1/2$ and $p = 0$ that correspond approximately to the Ohmic and super-Ohmic baths in the golden rule approach to relaxation.

Taking the initial state to be prepared in the higher-lying electronic state, electronic population of the higher electronic state as a function of time is shown on Fig. 1.

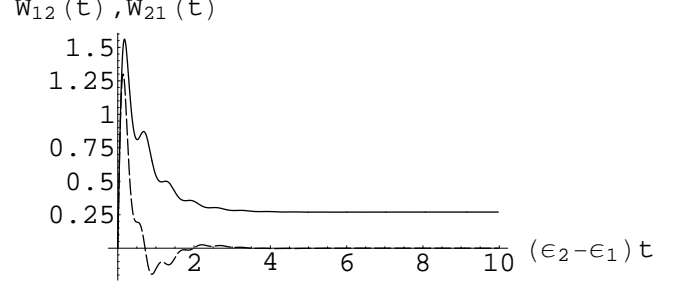


FIG. 2: Transition rates $W_{12}(t)$ and $W_{21}(t)$ for the super-Ohmic model

It can be seen that the relaxation does not follow a simple exponential decay. This behavior can be understood by looking at the explicit form of the rate coefficients $W_{12}(t)$ and $W_{21}(t)$ as functions of time as shown on Fig. 2 for the super-Ohmic case. Only after the rate coefficients become nearly constant in time does exponential relaxation occur. For the chosen parameter values, substantial non-exponential relaxation occurs before that time. Note the for the chosen parameters the complete electronic relaxation occurs before the onset of any possible recurrence phenomena due to the finite number of modes. Such recurrences will occur at the time scale of the order of 2π divided by the smallest normal mode frequency. It can also be seen on Fig. 2 that coefficients $W_{12}(t)$ and $W_{21}(t)$ can acquire negative values. This is in contrast to the golden rule approach where the coefficients are always positive and time independent. Because of the time dependence of coefficients $W_{12}(t)$ and $W_{21}(t)$ and their approximate nature the time-convolutionless master equation is not guaranteed to preserve the positivity of probabilities. Fig. 2 also shows the electronic relaxation for the Ohmic model obtained by applying the golden rule to the Hamiltonian (1) when coefficients g_{nmi} are treated on the same basis as g_{nmi} ($n \neq m$). No reliable golden rule results can be obtained for the super-Ohmic case because of the relatively small number of modes in the model.

B. Exciton regeneration at a semiconductor interface

As another example we consider the electronic relaxation in the conjugated polymer heterojunctions previously investigated in Ref. [10, 11, 12] by a different approach. Here we consider the decay of an excitonic state into a charge-separated state at the interface between two semiconducting polymer phases (TFB) and (F8BT). Such materials have been extensively studied for their potential in organic light-emitting diodes and organic photovoltaics [13, 14, 15]. At the phase boundary, the ma-

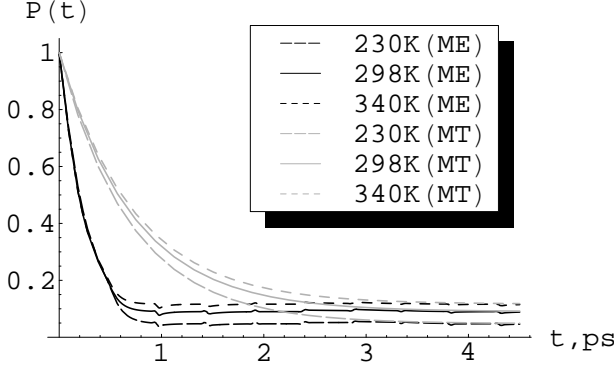
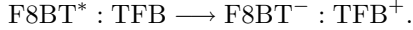
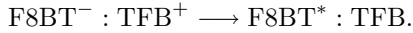


FIG. 3: The population of the excited state as a function of time for the TFB:F8BT heterojunction for three different temperatures obtained by solving the time-convolutionless master equation (ME) or through the Marcus-type approximation (MT).

terial forms a type-II semiconductor heterojunction with the off-set between the valence bands of the two materials being only slightly more than the binding energy of an exciton placed on either the TFB or F8BT polymer. As a result, an exciton on the F8BT side will dissociate to form a charge-separated (exciplex) state at the interface.



Ordinarily, such type II systems are best suited for photovoltaic rather than LED applications. However, LEDs fabricated from phase-segregated 50:50 blends of TFB:F8BT give remarkably efficient electroluminescence efficiency due to *secondary* exciton formation due to the back-reaction



as thermal equilibrium between the excitonic and charge-transfer states is established. This is evidenced by long-time emission, blue-shifted relative to the emission from the exciplex, accounting for nearly 90% of the integrated photo-emission.

Here, as above, we consider only two lowest electronic levels corresponding to

$$|XT\rangle = \text{F8BT}^* : \text{TFB} \text{ \& \ } |CT\rangle = \text{F8BT}^- : \text{TFB}^+.$$

As was shown in Ref. [16, 17, 18] for such systems there are two groups of phonon modes that are coupled strongly to the electronic degrees of freedom as evidenced by their presence as vibronic features in the vibronic emission spectra, namely: low frequency torsional modes along the backbones of the polymer and higher frequency C=C stretching modes. The normal modes within each group have about the same frequencies and form two separated bands. The interested reader is referred to Ref. [16, 17, 18] for specific details regarding the parameterization of the model.

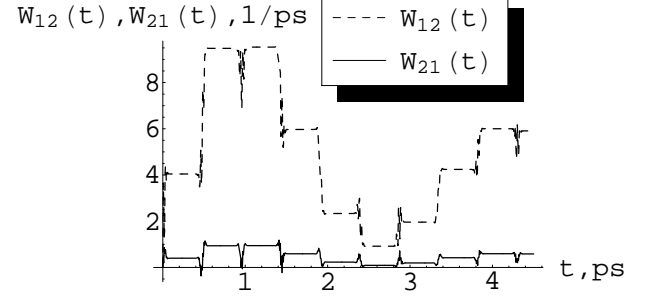


FIG. 4: Transition rates $W_{12}(t)$ and $W_{21}(t)$ for the TFB:F8BT heterojunction (see Ref. [10] for the model details) involving 24 normal modes at 298 K.

As before, we consider the initial state as being prepared in the $|XT\rangle$ state corresponding to photoexcitation of the F8BT polymer. The results for the higher electronic level population obtained by numerically solving Eq. (18) are shown on Fig. 3. The time dependence of coefficients $W_{12}(t)$ and $W_{21}(t)$ is shown on Fig. 4. As in the previous example the electronic relaxation does not follow a simple exponential pattern. The main difference between this model and the previous example is that the electronic relaxation time is of the same order as the recurrence time for coefficients $W_{12}(t)$ and $W_{21}(t)$. As can be seen from Fig. 4 the time dependence of these coefficients has the form of approximately constant regions abruptly changed at regular recurrence intervals. This type of time dependence makes the electronic relaxation look like a series of exponential relaxations with changing rates. As in the previous example, coefficients $W_{12}(t)$ and $W_{21}(t)$ can become negative as the relaxation proceeds towards the equilibrium population.

Note also, that because the relaxation does not obey a simple exponential rate law, the initial decay slightly “overshoots” the final equilibrium population. This is most evident in the highest temperature case considered here ($T = 340\text{K}$). Since the $|XT\rangle$ is also the emissive state, photo-emission (not included herein) depletes this population on a nanosecond time scale (radiative lifetime). Population back-transfer from the $|CT\rangle$ to maintain a thermal equilibrium population then leads to the continuous replenishment of the emissive species such that nearly all of the CT population contributes to the formation of secondary (regenerated) excitonic states [10, 11, 12, 13, 14, 15].

It is of interest to compare the relaxation dynamics in TFB:F8BT heterojunction obtained through the application of the time-convolutionless master equation with other approaches. As an example we will consider the Marcus-type approach which is widely used to study electron transfer in chemical systems [2, 11, 19, 20]. Because of the coordinate dependency of the coupling, some

care must be taken in deriving the Marcus rates and we give details of this in the appendix. The results for the relaxation dynamics using these rates applied to TFB:F8BT heterojunction for three different temperatures are shown in Fig. 3. It can be seen that apart from a more complicated time dependence the master equation approach gives faster relaxation when compared to the Marcus-type picture. The discrepancy between the two approaches can be explained by the fact that the Marcus approximation is assumed to be valid when $kT \gg \hbar\omega_i$ for all the normal modes. In the case of the TFB:F8BT heterojunction this condition is not satisfied for the higher frequency modes.

V. CONCLUSIONS

We derived the explicit form of the time-convolutionless master equation for the electronic populations in the electron-phonon systems. We applied it to study the electronic relaxation in the two-level electronic systems coupled to the Ohmic and super-Ohmic baths, as well as in the realistic conjugated polymer heterojunction. The time evolution of the electronic populations is, in general, more complex than the one obtained with the Pauli master equation and depends on the explicit form of the time dependent coefficient. The time-convolutionless master equation can account for the appearance of recurrence effects in smaller electron-phonon systems.

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APPENDIX: DERIVATION OF MARCUS-TYPE RATE EXPRESSIONS

To apply the Marcus approach for the system at hand, it is convenient to rewrite Hamiltonians (2) and (3) in terms of the coordinate q_i and momentum p_i operators for the normal modes as

$$H_0 = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{ni} \tilde{g}_{nni} |n\rangle\langle n| q_i + \sum_i \frac{p_i^2}{2} + \sum_i \frac{\omega_i^2 q_i^2}{2} \quad (\text{A.1})$$

and an off-diagonal part V

$$V = \sum'_{nmi} \tilde{g}_{nmi} |n\rangle\langle m| q_i, \quad (\text{A.2})$$

where

$$\tilde{g}_{nmi} = \sqrt{2\omega_i} g_{nmi}. \quad (\text{A.3})$$

The coordinate and momentum operators are then treated as static parameters and the rate constants for the transition from state $|n\rangle$ to state $|m\rangle$ is given by averaging the golden rule transition rates over the initial equilibrium distribution of the coordinates corresponding to the equilibrium ensemble for Hamiltonian H_0 assuming that the electronic state of the system is $|n\rangle$ [2], i.e.,

$$k_{nm} = 2\pi \int d\{q_i\} f(\{q_i\}) |V_{nm}(\{q_i\})|^2 \delta(U_n(\{q_i\}) - U_m(\{q_i\})), \quad (\text{A.4})$$

where $\{q_i\}$ denotes all coordinate variables and

$$f(\{q_i\}) = \frac{1}{Z} e^{-\beta U_n} \quad (\text{A.5})$$

and

$$V_{nm}(\{q_i\}) = \sum_i \tilde{g}_{nmi} q_i. \quad (\text{A.6})$$

Here Z is the partition function and U_n is given by

$$\epsilon_n + \sum_i \tilde{g}_{nni} q_i + \sum_i \frac{\omega_i^2 q_i^2}{2}. \quad (\text{A.7})$$

Note that Eq. A.4 differs from the similar expression of Ref. [2] by the presence of coordinate dependence in the interaction parameters $V_{nm}(\{q_i\})$. The integrations in Eq. A.4 can be explicitly performed giving

$$k_{nm} = \left(\left(\frac{\Delta E_{nm} P_{nm}}{E_{nm}^\lambda} + F_{nm} \right)^2 - \frac{2G_{nm}^2}{\beta E_{nm}^\lambda} + \frac{H_{nm}}{\beta} \right) \times \sqrt{\frac{\pi\beta}{E_{nm}^\lambda}} \exp \left(-\frac{\beta(\Delta E_{nm} - E_{nm}^\lambda)^2}{4E_{nm}^\lambda} \right). \quad (\text{A.8})$$

Here ΔE_{nm} and E_{nm}^λ are given by

$$\Delta E_{nm} = \epsilon_n - \epsilon_m - \sum_i \frac{\tilde{g}_{nni}^2}{2\omega_i^2} + \sum_i \frac{\tilde{g}_{mmi}^2}{2\omega_i^2}, \quad (\text{A.9})$$

$$E_{nm}^\lambda = \sum_i \frac{(\tilde{g}_{nni} - \tilde{g}_{mmi})^2}{2\omega_i^2} \quad (\text{A.10})$$

and are usually referred to as the driving force and reorganization energy, respectively. Parameters P_{nm} , F_{nm} , and H_{nm} are given by

$$P_{nm} = \frac{\tilde{g}_{nmi}(\tilde{g}_{nni} - \tilde{g}_{mmi})}{2\omega_i^2}, \quad (\text{A.11})$$

$$F_{nm} = \frac{\tilde{g}_{nmi}(\tilde{g}_{nni} + \tilde{g}_{mmi})}{2\omega_i^2}, \quad (\text{A.12})$$

$$H_{nm} = \frac{\tilde{g}_{nmi}^2}{\omega_i^2}. \quad (\text{A.13})$$

It can be verified from Eqs. (A.4) or (A.8) that rates k_{nm} satisfy the principle of the detailed balance, i. e.,

$$\frac{k_{nm}}{k_{mn}} = e^{\beta \Delta E_{nm}}. \quad (\text{A.14})$$

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